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H. F. Shaw
S. Niemeyer
G. F. Hunt

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H. F. Shaw, S. Niemeyer, and G. F. Hunt
Nuclear Chemistry Division, L-232
P. O. Box 808
Lawrence Livermore National Laboratory
Livermore, California 94550, USA

ABSTRACT

An efficient and reliable method of focusing the source of a thermal ionization mass spectrometer while under computer control has been developed. The focusing program uses a simplex algorithm which is easily programmed and does not require knowledge of the form of the function being maximized. This algorithm focuses at least as reliably as an experienced operator, and usually in less time than that required for careful manual focusing, and thus represents a significant improvement over previous automated focusing techniques.

INTRODUCTION

The development of a new generation of computer-controlled, thermal-ionization mass spectrometers capable of automated operation has created a need for a means of computerized optimization of the focus parameters of a spectrometer's source during an analysis. In this communication we describe an efficient and reliable, automated focusing method based on the simplex algorithm [1].

The ion source of a thermal ionization mass spectrometer contains an electrostatic lens which collects the ions emitted from the surface of a hot filament, accelerates them, and focuses them prior to entry into the analyzer section of the instrument. A typical lens consists of several plates, including one or more pairs of half plates that steer the beam, held at potentials determined by the design of the lens. Due to variations among the filaments and sample loads, some adjustment of the plate potentials is required for each filament in order to achieve optimum focusing conditions. In addition, focusing conditions often change during the course of an analysis. Under normal circumstances, the optimum focusing condition is defined as that which maximizes the number of ions collected at the detector. In order to fully utilize the capabilities of an automated mass spectrometer, some means must be found to carry out this focusing procedure while under computer control.

The simplest approach would be to exhaustively search all possible combinations of the focus parameters. This method, however, would clearly require an impractical amount of time. Our instrument has seven adjustable parameters and if each parameter were limited to only ten possible settings and allowing 0.5 sec for each measurement of the beam intensity, it would take nearly four months to focus the source. We require that the automated procedure not take significantly more time than focusing by an experienced operator.

The next simplest approach is to individually optimize each focusing potential in turn. This is a commonly-used solution. Unfortunately, there is considerable interaction between the potentials: changing the voltage of one plate changes the optimal settings of the other plates. Thus, the order in which adjustments are made can drastically alter the "best" focusing conditions determined by this method. Repeated iteration of this method would in principle result in convergence regardless of the order in which the parameters are adjusted; however, convergence is slow. A more serious drawback to this technique is the fact that there are commonly several focusing conditions that yield local maxima in the detected ion current. If the initial estimate of the focusing conditions is far from optimal, adjusting one parameter at a time often results in optimization about a local maximum rather than the absolute maximum corresponding to the best focus. Our experience has shown that these problems are minimal when using triple filament techniques. However, many of the elements analyzed in our research are run using single filaments and, in these cases, sequentially optimizing each focus parameter while under computer control fails to find the optimum focusing conditions over 50% of the time, and in many cases this automatic focusing gives less than half the beam current obtained manually. Clearly, some more reliable means of focusing is desirable. Our goal is to devise a focusing algorithm which yields a measured beam current that is at least 95% of the beam current obtained by manual focusing by an experienced operator.

MAXIMIZATION TECHNIQUES

The process of adjusting N focus parameters to maximize the beam current is mathematically equivalent to the problem of finding the extremum of a function with N independent variables. Such problems are commonly encountered in applied mathematics, e.g. solving nonlinear least-squares problems, and a variety of mathematical methods have been devised to solve these problems [1]. The focusing technique discussed above, utilizing successive optimization of each focus parameter in turn, corresponds to the mathematical method of stepwise descent (ascent in this case). As noted, this method is slow to converge when there is significant correlation among the parameters. Other mathematical techniques such as the steepest descent, Newton-Ralphson or Marquardt algorithms converge more rapidly, but require knowledge of the first or second partial derivatives of the function being maximized with respect to the independent parameters. In the present case, the functional form of the response surface is unknown, i.e. we do not know *a priori* how the ion beam intensity will vary at the detector as the focusing potentials are varied. The partial derivatives would need to be approximated by finite differences, entailing the measurement of several points on the response surface for each iteration with a consequent loss in speed. In addition, these methods may diverge, are subject to truncation errors, involve a large number of matrix operations, and require rather large computer codes. Finally, all these methods search only a limited region of the parameter space and are thus liable to converge to the first local extremum encountered. Use of the simplex algorithm avoids most of these problems.

SIMPLEX ALGORITHM

The simplex algorithm is a relatively new technique for finding the extrema of functions [1, see 3 for an annotated bibliography of applications of the simplex algorithm]. A simplex is a geometric figure with n+1 vertices, where n is the dimensionality of the space in which the simplex is defined. A simplex on a plane (n=2) is thus a triangle. Each vertex of the simplex is characterized by n+1 numbers: the n coordinates of the vertex in the parameter space, $\hat{V}_i = (a_1, a_2 \ldots a_n)$, and the response (value of the function being maximized), R_i at $\hat{V}_i$. The maximum of the function is found by moving the simplex uphill according to a few simple rules that replace the vertex having the worst response with a new vertex. New vertices are generated by one of four operations: reflection, expansion, contraction, and shrinkage. Figure 1 shows the effects of these operations on a two-dimensional simplex.

In what follows, it may be useful to refer to Fig. 2, which is an outline of the simplex algorithm in flowchart form. The initial simplex is formed by picking n+1 vertices that span the region of parameter space of interest. The vertices with the best ($\hat{V}_B$) and worst ($\hat{V}_W$) responses (R_B and R_W, respectively) are identified, in the case at hand, by measuring the ion beam intensity at the focus setting represented by each vertex vector. The algorithm then finds a reflected vertex, $\hat{V}_R$, by reflecting the worst vertex through the center of all the other vertices:

$$\hat{V}_R = \hat{M} \bullet (1+\alpha) - \alpha\hat{V}_W, \qquad (\alpha>0)$$

where

$$\hat{M} = \sum_{I\neq \text{worst}} \hat{V}_i/N$$ is the center of all vertices excluding the worst.

The response R_R at $\hat{V}_R$ is then measured. If $R_B > R_R \geq R_W$ then $\hat{V}_W$ is replaced by $\hat{V}_R$ and the procedure starts over with this new simplex. If $R_R \geq R_B$, the routine tests the response, R_E, at an expanded vertex, $\hat{V}_E$, formed by moving $\hat{V}_R$ further along the line connecting $\hat{M}$ and $\hat{V}_W$:

$$\hat{V}_E = \beta \bullet \hat{V}_R + (1-\beta) \bullet M, \qquad (\beta>1)$$

If $R_E \geq R_B$ the expanded vertex is accepted and the algorithm restarted. If $R_E < R_B$ the expanded vertex is rejected and $\hat{V}_W$ is replaced by $\hat{V}_R$. If, upon reflection, $R_R < R_W$ a contracted vertex is formed:

$$\hat{V}_C = \gamma\hat{V}_W + (1-\gamma)\hat{M} \qquad (0<\gamma<1)$$

$\hat{V}_W$ is replaced by $\hat{V}_C$ and the routine restarted, unless $R_C < R_W$. In this case, all vertices are replaced by the shrunken vertices, $(\hat{V}_i + \hat{V}_B)/2$, and the process restarted. This sequence is repeated until convergence. Figure 3 shows the movement of a two-dimensional simplex on a simple response surface.

The parameters α, β, γ govern how much the volume of the simpex is changed in one iteration. In general, the values $\alpha=1$, $\beta=2$, $\gamma=1/2$ yield the best results [1], Nonlinear constraints on the parameters, such as $0 < a_i < 1$, are easily incorporated into the algorithm by assigning very poor responses to vertices that lie outside the acceptable range of parameter values. This feature is useful for our application as each lens potential is only capable of varying over a limited range. The main features of the simplex method are summarized below:

1. Only a few measurements of the response are needed for each iteration.
2. No knowledge of derivatives is required.

3. No matrix operations are involved.
4. Divergence is impossible.
5. Convergence is relatively rapid. (Iterations to convergence is proportional to $(n+1)^2$.
6. Nonlinear constraints are easily incorporated.
7. A large portion of parameter space can be explored by a judicious choice of initial vertices.
8. The algorithm is simple to understand and easy to program.

IMPLEMENTATION AND RESULTS

We have incorporated a simplex-based focusing routine into the control program for our VG354* mass spectrometer. This program is written in Hewlett Packard BASIC running on a Hewlett Packard 9845B computer. The mass spectrometer utilizes a thin lens source with seven independently-adjustable potentials for focusing purposes. Computer control of the focusing potentials is achieved by individual programmable power supplies for each lens. From experience, we have found that portions of the possible range of several of the parameters never yield optimal focusing conditions, so the range over which these parameters can vary in the simplex routine has been limited by assigning very low responses to vertices that lie outside the acceptable range. By limiting the size of parameter space in this way, the simplex spends less time exploring unprofitable regions of parameter space and converges to the optimal focus more quickly.

We have also noted that there is little interaction between the value of the Z-bias focus parameter, which steers the beam in a direction perpendicular to the magnet pole pieces, and the other parameters. Our

*VG Instruments, Stamford, CT 06901.

instrument is, however, equipped with a rotatable, 16-sample turret. Small angular displacements of the turret act to physically move the filament in a direction perpendicular to the magnet pole pieces. Thus, to some extent, the effect of changing the Z-bias potential can be duplicated by a small rotation of the turret. For these reasons, we do not include the Z-bias potential in the simplex optimization. Instead, it is optimized using the stepwise ascent method (see above) after optimization of the other six parameters and after rotation of the turret to find the position that maximizes the detected ion current when the Z-bias is set to a neutral position (no deflection). Turret optimization is normally carried out only once for each sample when the beam current has reached at least 10% of the current at which data is taken.

The same initial simplex is used for every sample. The initial vertices were chosen to lie in regions of parameter space that, from experience, were known to often yield good focusing conditions. In subsequent calls to the focusing routine the optimum focus parameters determined by the previous call are substituted for the closest vertex in the initial set.

The simplex is considered to have converged if the beam intensity at each vertex is within 5% of the intensity of the best vertex <u>and</u> if the value of each parameter of each vertex is within 100 units (out of a total range of 1000 units) of the corresponding parameter of the best vertex. Convergence usually occurs within 50 iterations during the first call to the focusing routine and typically requires 35 iterations for subsequent calls. The time required is on the order of three minutes. These convergence criteria are relatively liberal but are normally sufficient to focus to within 5% of the beam intensity of the absolute maximum. Rather than adopt a more restrictive definition of convergence, we find it more efficient to use the stepwise ascent method, starting with the Z-bias potential, to "fine tune" the focusing conditions determined by the simplex method. An additional increase of ~5% in ion current is typically obtained by this procedure.

In order to save time, the beam intensity is not measured at every vertex during every iteration. Changes in the beam intensity due to growth or decay of the number of ions emitted from the filament are adequately accounted for by measuring the response at every vertex during every tenth iteration provided the rate of change is not excessive (see Fig. 2). Beam intensities are measured with a 0.2-sec integration period. A settling time of 0.3 sec after changing focus potentials is allowed before measuring the beam current so that the lens plates can reach their proper potentials. The simplex focusing routine has been evaluated over a period of several months during which time a wide variety of elements have been analyzed including: U, Th on triple filaments; NdO, Sm, Re on single Re filaments; Sr, Cs, TiO on single oxidized Ta filaments; and Rb on single Re filaments using a silica gel emitter. For 43 samples we compared the beam intensity obtained by automated simplex focusing with that obtained by an experienced operator. In 34 cases the simplex-determined focus conditions yielded an intensity within 5% of that obtained by the operator. In seven cases the simplex found a significantly better focus than did the operator (>105% of the "manual" intensity) and in two cases the simplex method resulted in an intensity between 90 and 95% of that obtained by the operator. We consider these results to be quite satisfactory, demonstrating that in the great majority of cases, the simplex technique results in focusing conditions better than or equal to that achieved by careful manual focusing.

The simplex technique also appears to be relatively insensitive to the existence of local maxima in the response surface. In every case tested, the simplex converged to the absolute maximum in beam intensity. Further, the optimal focus often changes position in parameter space over the course of a run, resulting in a new absolute maximum in beam intensity at a focus position far from the previous optimal conditions. The simplex technique has no difficulty tracking these changes in focus conditions.

In conclusion, we believe that the method of automated focusing described here is a significant improvement over focusing methods based on stepwise ascent techniques. This advance makes it possible to utilize a computer-controlled mass spectrometer in an automated mode with full confidence that analytical performance will not be degraded by less than optimal focusing. The algorithm focuses at least as reliably as an experienced operator, usually accomplishes this in less time than that required for careful manual focusing, and is easy to both understand and program.

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REFERENCES

1. J. A. Nelder and R. Mead, Computer J. 7 (1965) 308.
2. P. R. Adby and M.A.H. Dempster, Introduction to Optimization Methods, London: Chapman and Hall (1974).
3. S. N. Deming and S. L. Morgan, Anal. Chem. Acta. 150 (1983) 183.

FIGURE CAPTIONS

Fig. 1. A two-dimensional simplex ($\hat{V}_B\hat{V}_W\hat{V}_I$) showing the effects of the basic simplex operations. $\hat{V}_B$ = best vertex, $\hat{V}_W$ = worst vertex, $\hat{V}_I$ = intermediate vertex, $\hat{V}_R$ = reflected vertex, $\hat{V}_E$ = expanded vertex, $\hat{V}_C$ = contracted vertex, and $\hat{V}_S$ = shrunken vertices.

Fig. 2. Flowchart of the simplex algorithm as implemented in the mass spectrometer focusing routine. R_R, R_E, R_C, R_B, R_W refer to the responses (ion currents) at the reflected, expanded, contracted, best, and worst vertices. I1, I2 are iteration counters. See text.

Fig. 3. Movement of a simplex on a two-dimensional response surface.

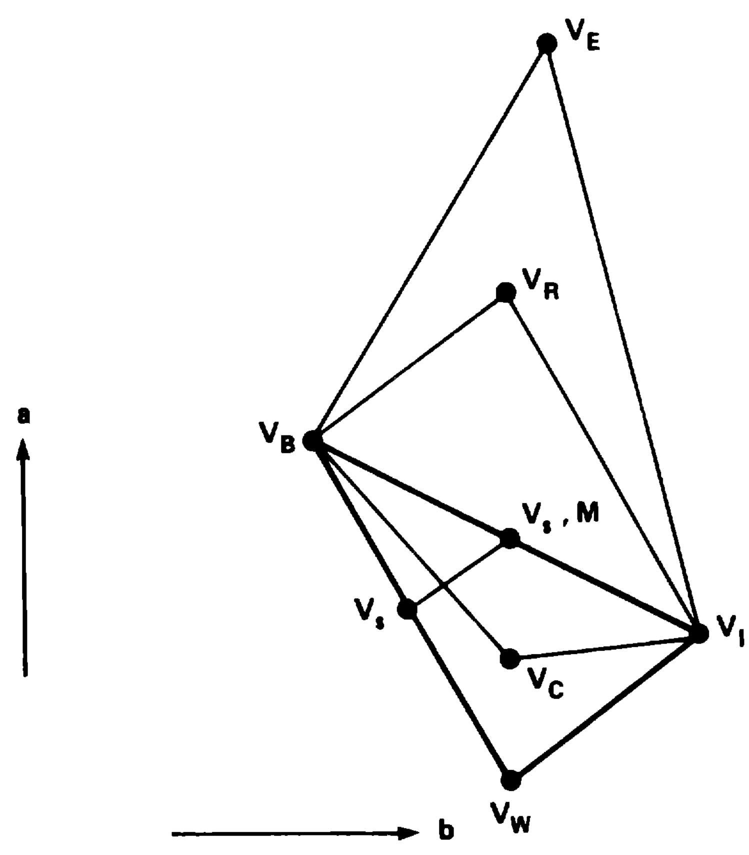

Fig 1.

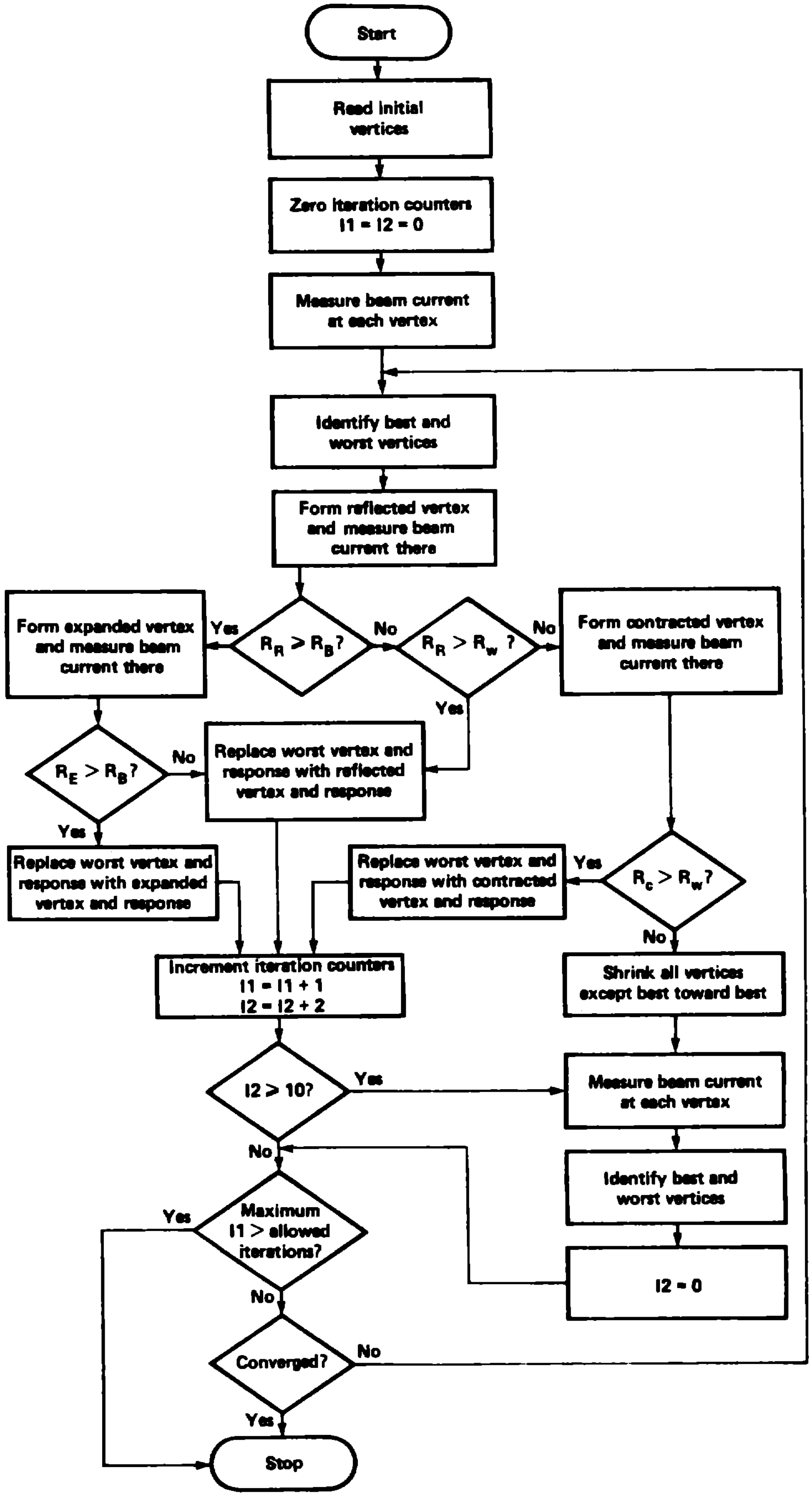
Start
Read initial vertices
Zero iteration counters
I1 = I2 = 0
Measure beam current at each vertex
Identify best and worst vertices
Form reflected vertex and measure beam current there
$R_R > R_B$?
Yes
No
Form expanded vertex and measure beam current there
$R_R > R_W$?
No
Yes
Form contracted vertex and measure beam current there
$R_E > R_B$?
No
Yes
Replace worst vertex and response with reflected vertex and response
Replace worst vertex and response with expanded vertex and response
Replace worst vertex and response with contracted vertex and response
Yes
$R_c > R_w$?
No
Increment iteration counters
I1 = I1 + 1
I2 = I2 + 2
Shrink all vertices except best toward best
I2 > 10?
Yes
No
Measure beam current at each vertex
Identify best and worst vertices
Yes
Maximum I1 > allowed iterations?
No
I2 = 0
Converged?
No
Yes
Stop

Fig. 2

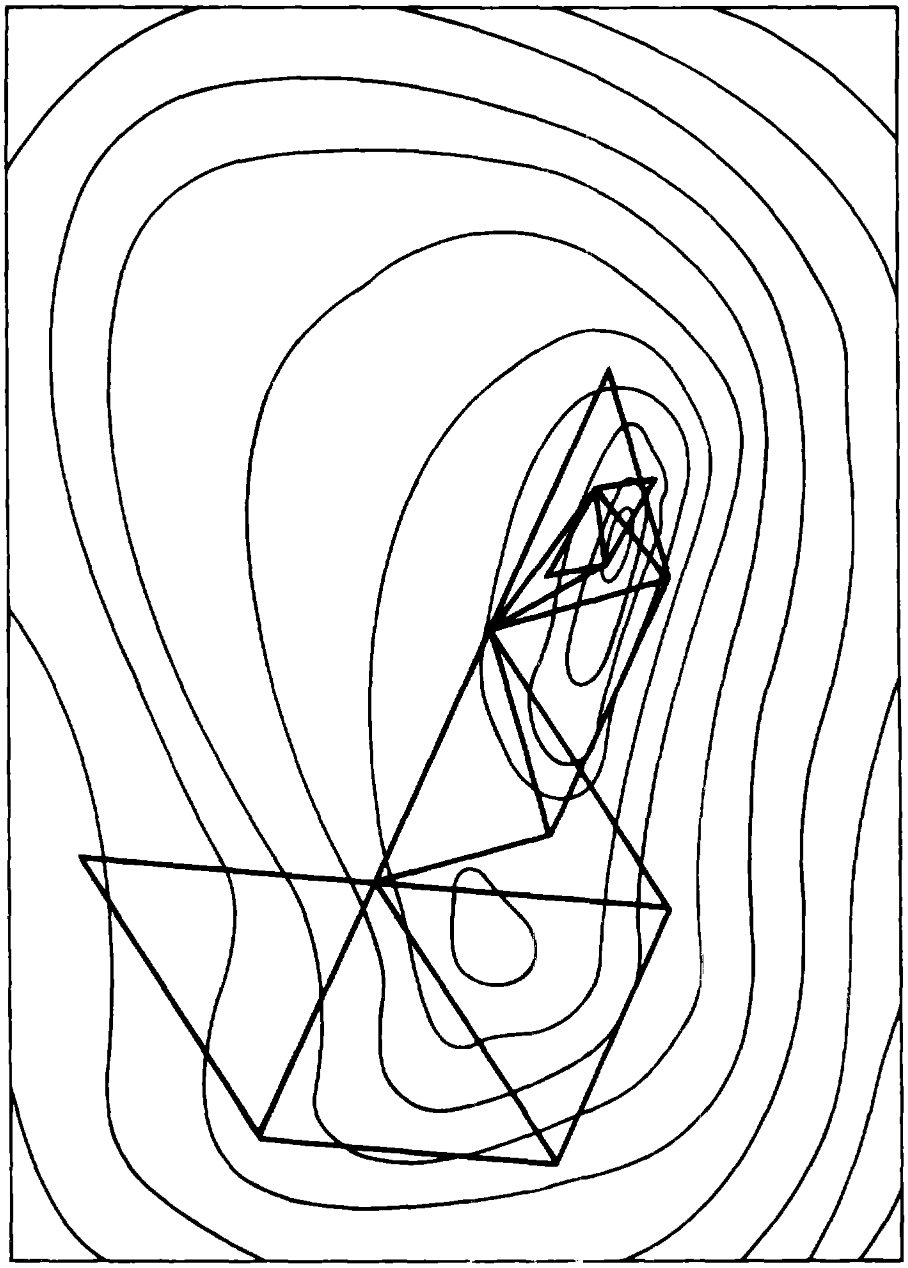

Fig. 3